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IMPROVED ANODIC STRIPPING VOLTAMMETRIC PROCEDURE FOR POLLUTION MONITORING OF TRACES OF LEAD THROUGH IN-SITU SODIUM DEPOSITION

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ABSTRACT

A simple, rapid and reliable linear sweep anodic stripping voltammetric procedure is described for the determination of trace amounts of lead. The sensitivity of the procedure is improved by one magnitude by incorporating in-situ sodium deposition for the first time on preformed mercury film glassy carbon electrode. The sensitivity of the procedure is further enhanced by 2 fold by incorporation of tetraalkyl ammonium salt to the acetate buffered chloride medium arising out of the synergistic effect. The developed procedure is suitable for the pollution monitoring of 10^{-7} to 10^{-4} M of lead present in drinking and sea water samples.

Key words: Anodic stripping voltammetry, in-situ sodium deposition, pollution monitoring of Pb

INTRODUCTION

Anodic Stripping Voltammetry [1] (ASV) is a well known technique in pollution monitoring of various inorganics, particularly heavy metals. Various attempts have been made over the years in order to improve the sensitivity and selectivity of the ASV procedures. One such approach involves the introduction of sophisticated electro-analytical techniques [2, 3] like phase selective alternating current, normal and differential pulse methods in place of simple linear scan in ASV method. Other approaches include the nature and geometry of electrode material [1], prior chemical preconcentration [4] or in-situ deposition [5, 6].

First attempt in improving the sensitivity is made as early as 1968, whereby incorporation of in-situ ammonium deposition, the sensitivity of the ASV procedure is improved by one magnitude by utilizing HMDE as working electrode [5]. Similar enhancement in sensitivity is reported by incorporation of in-situ sodium deposition during the determination of cadmium utilizing same HMDE [6]. This paper for the first time evaluates the potentialities of in-situ sodium deposition on mercury film electrode by taking the determination of lead as an example.

EXPERIMENTAL

Reagents

All solutions were prepared using analytical grade reagents and conductivity water.

Lead (II) solution
Acetate buffer, 1 M (pH 5.0)
Sodium chloride solution, 5 M
Tetramethyl ammonium chloride, 1 M

Apparatus

Voltammetric studies were carried out using a Wenking mode 75 M potentiostat and Wenking scan generator, using a three electrode cell assembly; a normal calomel reference (1 M KCl) a platinum foil counter and a glassy carbon (Tokai & Co. 3 mm dia) working electrodes. The recordings were made on a Digilog XY-recorder.

Procedure

Preparation of mercury film on glassy carbon electrode (GCE)

The glassy carbon surface is freshly polished with emery papers of increasing fineness i.e. grades 1/0 to 4/0 and the mercury film is formed as described elsewhere [7].

Determination of lead in drinking or sea water

Transfer a suitable aliquot (up to 35 ml) of sample solution containing 20 ppb to 20 ppm of lead into 50 ml volumetric flask and 5 ml of acetate buffer and tetramethylammonium chloride and 2.5 ml of sodium chloride solution and dilute to volume with water. Transfer the solution into the electrochemical cell and place the mercury film coated glassy carbon electrode (MFGCE) in it. Deposit for 2 min. at − 1.4 V vs NCE with stirring. Switch off the stirrer. Allow 30 seconds for the turbulence to cease and anodically scan the potential from − 1.4 to 0.5 V at a sweep rate of 270 mV/s. Establish the concentration of lead by standard addition technique by following the above mentioned procedure.

RESULTS AND DISCUSSION

Fig. 1 shows the stripping voltammograms obtained after depositing at − 1.6 V for 2 min. on MFGCE from 0.1 M tetramethyl ammonium chloride (curve A), 0.1 M tetramethyl ammonium chloride + buffered sodium chloride (curve B) and 0.1M tetramethylammonium chloride + buffered sodium chloride + 100 ppb of lead (curve C). As clear from the figure, the sodium dissolution peak occurs at − 1.2V and that of lead at − 0.51 V vs NCE.

Two separate experiments were carried out to investigate the effect of in-situ deposition and the utilization of mixed supporting electrolyte on the sensitivity. The stripping signal of lead is doubled on including in-situ deposition of sodium when the deposition potential is restricted to − 1.1 V and − 1.4 V as seen from fig. 2.

Fig. 3 clearly shows the synergistic enhancement in stripping signal of lead by utilizing tetraethylammonium chloride and buffered sodium chloride with and without in-situ sodium deposition (curves C and D respectively) compared to those obtained when they are present individually (curve A or B). Hence use of both the mixed supporting electrolyte and in-situ sodium deposition were to obtain maximum sensitivity during the optimization of various analytical parameters for the determination of lead.

Effect of deposition potential

In order to ascertain the optimum deposition potential (E_d), the cathodic limit of deposition potential is varied in the range − 1.1 to − 1.6 V in steps of 0.1 V with 2 min. deposition at each E_d followed by linear scan anodic stripping. As seen from Table I, the magnitude of stripping signal attains maximum at − 1.3V vs NCE and remains unaltered on changing to more negative potentials.

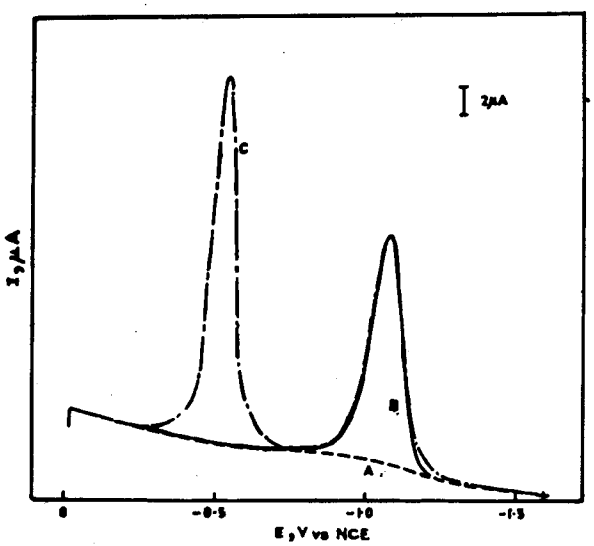

Fig. 1: Anodic stripping voltammogramms (Depositition potential

$E_d = -1.6V$, time of deposition $t_d = 2$ min)

A – 0.1 M tetramethylammonium chloride

B – as in A with addition of 0.025 M acetate buffer (pH 5) and 0.25 M NaCl

C – as in B with addition of 100 ppb of lead

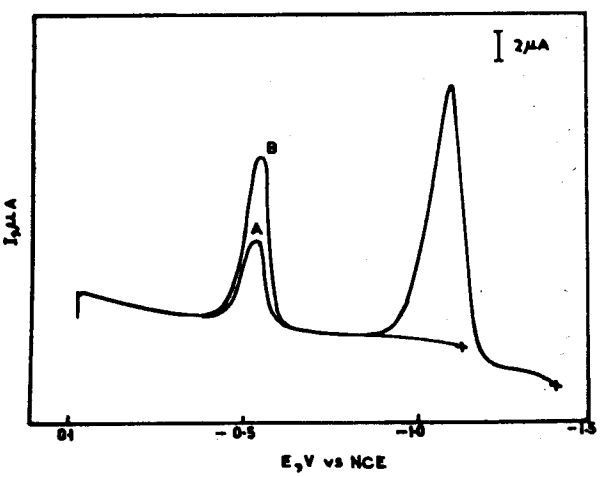

Fig. 2: Effect of in-situ sodium deposition in the stripping determination of lead with mercury film coated glassy carbon electrode, concentration of lead = 100 ppb, 0.025 M acetate buffer (pH 4.8), 0.25 M sodium chloride, total volume = 50 ml, t_d = 2 min. E_d = −1.1 V (curve A) and −1.4 V (curve B)

Table-I: Effect of deposition potential

(Pb (II) = 100 ppb, t_d = 2 min., v = 270 mV/s)

Deposition potential (V vs NCE)	I_p (μA)
−1.1	10.0
−1.2	14.5
− 1.3	24.0
−1.4	25.0
−1.5	25.5
−1.6	25.0

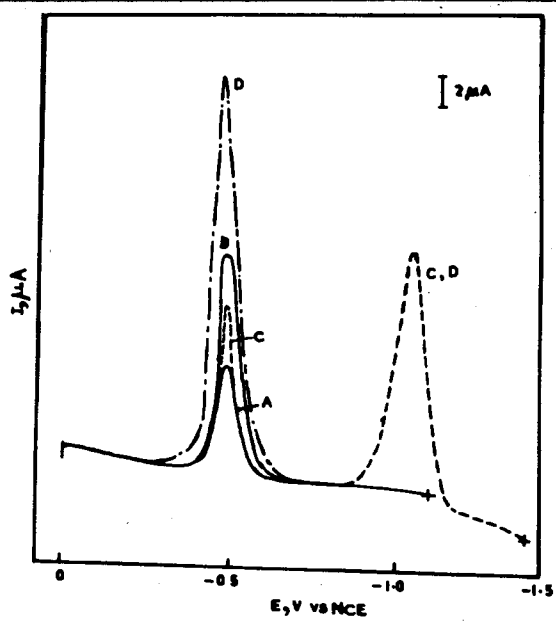

Fig. 3: Effect of mixed supporting electrolyte and in-situ sodium deposition in the anodic stripping voltammetric determination of lead, concentration of lead = 100 ppb, t_d = 2 min, total volume = 50 ml.

A – 0.1 M tetramethylammonium chloride, $E_d = -1.1$ V

B – As in A with acetate-buffered chloride without in-situ sodium deposition, $E_d = -1.1$ V

C – as in A with addition of acetate buffered NaCl; $E_d = -1.4$ V

D – as in B with in-situ sodium deposition, $E_d = -1.4$ V

Variation of sweep rate

Table II shows the anodic stripping currents obtained during the stripping of preconcentrated lead on MFGCE after deposition at − 1.4 V for 2 min. The maximum sensitivity is obtained in the sweep rate range 220 to 400 mV/s. A sweep rate of 270 mV/s is used in subsequent experiments. The stripping signal was found to be same for repetitive determinations.

Table-II: Effect of sweep rate

(Pb) (II) = 100 ppb, t_d = 2 min, $E_d = -1.4$ V)

Sweep rate (mV/s)	I_p (μA)
6	5.0
30	10.0
100	18.0
220	24.0
270	25.0
330	24.5
400	24.0

Sensitivity and precision

Under optimized conditions, the developed procedure is useful for determination of 0-20 ppm of lead with a detection limit of 10 ppb. The coefficient of variation for 0.1 ppm lead was found to be 0.5% for 5 replicate determinations.

Analysis of synthetic samples

Table III shows the results obtained on the analysis of synthetic sample solutions of open sea, deep sea and Great Salt Lake water compositions [8,9]

with known amounts of added lead. From the recoveries, it is clear that the developed procedure is suitable for the pollution monitoring of lead in a variety of sea water samples in addition to drinking water samples.

Analysis of sea water samples

Sea water samples collected form Bay of Bengal at Mandapam and Mallipatnam were subjected to the determination of lead by the procedure described in Experimental section. The recoveries obtained on addition of known amounts of lead are shown in Table IV. These results clearly demonstrate the usefulness of the developed procedure for pollution monitoring of lead in drinking and sea water samples as the safety limit of lead in drinking water is 50 ppb [10].

Table-III: Analysis of synthetic solutions

Pb (II) = 100 ppb, t_d = 2 min, E_d = −1.4 V, V = 270 mV/s

S. No.	Composition of the synthetic sample (%)	Aliquot taken (ml)	I_p (μA)
1.	None	–	25.0
2.	Sea water		
	Na (1.05), K (0.04)	20	24.5
	Mg (0.13), Ca (0.04)	45	24.8
	Cl (1.89)		
3.	Deep sea water		
	Na (3.2), K (0.64)	20	24.0
	Mg (3.67), Ca (1.3)	40	24.7
	Cl (17.0)		
4.	Great salt Lake water		
	Na (6.7), K (0.34)	20	24.8
	Mg (0.56), Ca (0.03)	40	24.9
	Cl (11.2)		

Table-IV: Analysis of sea water samples

S.No.	Aliquot taken (ml)	Amount of lead added (ppb)	Amount of lead recovered (ppb)	Recovery (%)
Sample I				
1	20	–	–	–
2	20	20	19.8	99
3	40	100	98.0	98
Sample II				
4	40	–	–	–
5	40	1000	1000.0	100
6	40	50	50.0	100

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